

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE April 125, 2003		3. REPORT TYPE AND DATES COVERED Final Report, 3/1/98-2/28/03
4. TITLE AND SUBTITLE Structure Property Relationships in Liquid Crystalline Thermosets			5. FUNDING NUMBERS G DAAG55-98-1-0114	
6. AUTHOR(S) Elliot P. Douglas				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Materials Science and Engineering Box 116400, University of Florida Gainesville, FL 32611			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER  37597.10-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  This report describes our work investigating structure property relationships in liquid crystalline thermosets (LCT's). Among the improved properties expected for LCT's compared to conventional thermosets are improved chemical resistance, resistance to environmental changes, and enhanced mechanical properties. The main objective for this work is to understand the relationships among molecular structure, phase transitions, curing behavior, and properties for these unique materials. The morphology of LCT's can be understood as a complicated interaction between the liquid crystalline order and the network structure, which are both in turn affected by molecular architecture and cure behavior. Relating these structural parameters to the resulting properties will provide the basic structure-property relationships. In particular, LCT's will exhibit behavior that is characteristic of both ordered liquid crystals and highly crosslinked thermosets. We have investigated the synthesis, cure behavior, thermal stability, mechanical properties and interaction with water.				
14. SUBJECT TERMS composite, thermoset, liquid crystal			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

Enclosure 1

## STATEMENT OF PROBLEM

Our objective for this project is to understand the relationship between molecular structure and physical properties in liquid crystalline thermosets (LCT's). In particular, we have measured the effects of changes in structure on thermal transitions, gelation, mechanical properties, and transport properties. Conventional thermosets, such as epoxies and vinyl esters, are used extensively as structural materials, adhesives, and in many other applications. Their use is limited, however, by their inherent brittleness, low strength, and permeability to gases and moisture. In contrast, liquid crystalline polymers (LCP's) are known for their high strength, good fracture toughness, and good barrier properties. LCT's combine the beneficial properties of LCP's with the processing advantages of conventional thermosets. Thus, LCT's have potential as a new class of thermoset materials with improved chemical resistance, resistance to environmental changes, and enhanced mechanical properties. For example, use of LCT's in composites will result in structures that are more damage tolerant, that have reduced weight with increased strength, and that can better resist environmentally induced failure. The molecular ordering inherent in a liquid crystalline phase could also lead to self-assembled structures based on LCT's that have novel electronic and optical properties. Thus, LCT's have the potential to be recognized as a new material with unique properties. This work provides the basis for understanding these properties.

## SUMMARY OF RESULTS

### LCT Monomers

Figure 1 shows the structures of the LCT's investigated during this project. These materials fall into two basic categories. The first are acetylene terminated LCT's, which were synthesized according to the scheme shown in Figure 2. A series of monomers were synthesized consisting of 12 different molecules, which are made up of two different mesogens and 6 different flexible tails. Characterization of the thermal transitions in the uncured monomers shows the expected trends: monomers with both long flexible tails and long mesogens exhibit both a nematic and a smectic phase; monomers with short tails and/or short mesogens exhibit only a nematic phase; and an odd-even effect is observed, in which the clearing temperatures as a function of tail length for the monomers with an odd number of carbons in the flexible tail lies on a curve higher than for the monomers with an even number of carbons in the tail. In addition to the monomers with flexible tails, a phenylacetylene terminated monomer (phBP, Figure 1) was synthesized using the same approach and its thermal stability was investigated (see Thermal Stability, below).

The other set of LCT's were epoxy thermosets. The primary epoxy investigated was diglycidyl ether of  $\alpha$ -methylstilbene (DOMS), cured with sulfanilamide (SAA). In the early stages of the project this was synthesized by us using standard literature procedures. Later a donation of this material was received from The Dow Chemical Company. DOMS is a monotropic liquid crystal that forms a smectic phase during cure. For certain applications, e.g. magnetic field processing, it may be desirable to have an enantiotropic nematic LCT. In addition, it is of fundamental interest to examine the phase behavior of epoxy oligomers of different lengths, and to compare the different properties of smectic and nematic LCT's. Therefore, we have investigated the synthesis of new LCT epoxy oligomers based on the reaction between aniline and DOMS (DxAy, Figure 1). The reaction of DOMS with aniline in different molar ratios leads to oligomers of different lengths. Our work so far has identified the reaction conditions, which are dioxane at reflux for 24 hours without a catalyst. In all cases there is an excess of DOMS to ensure that the oligomers have epoxide endgroups. Initial characterization indicates that the oligomer made from a 2:1 ratio of DOMS:aniline (the shortest oligomer made) exhibits a nematic phase from 83° to 135° C. Characterization of oligomers with other lengths is ongoing.

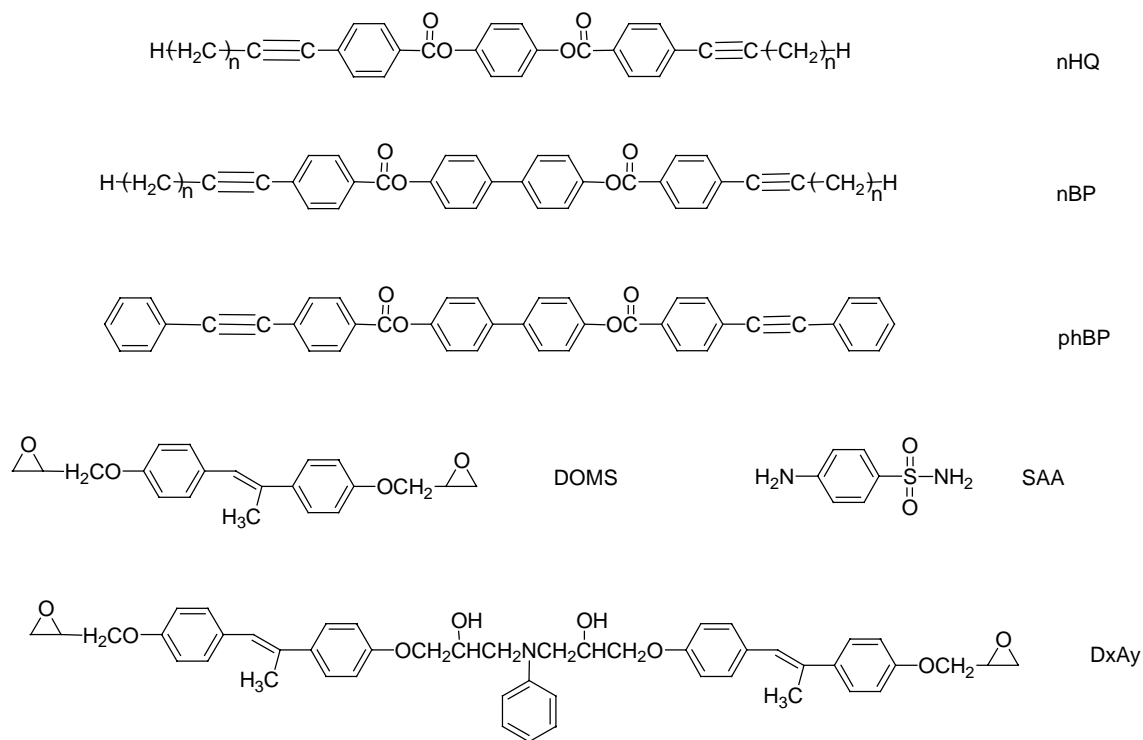


Figure 1: Structures of LCT's investigated in this project.

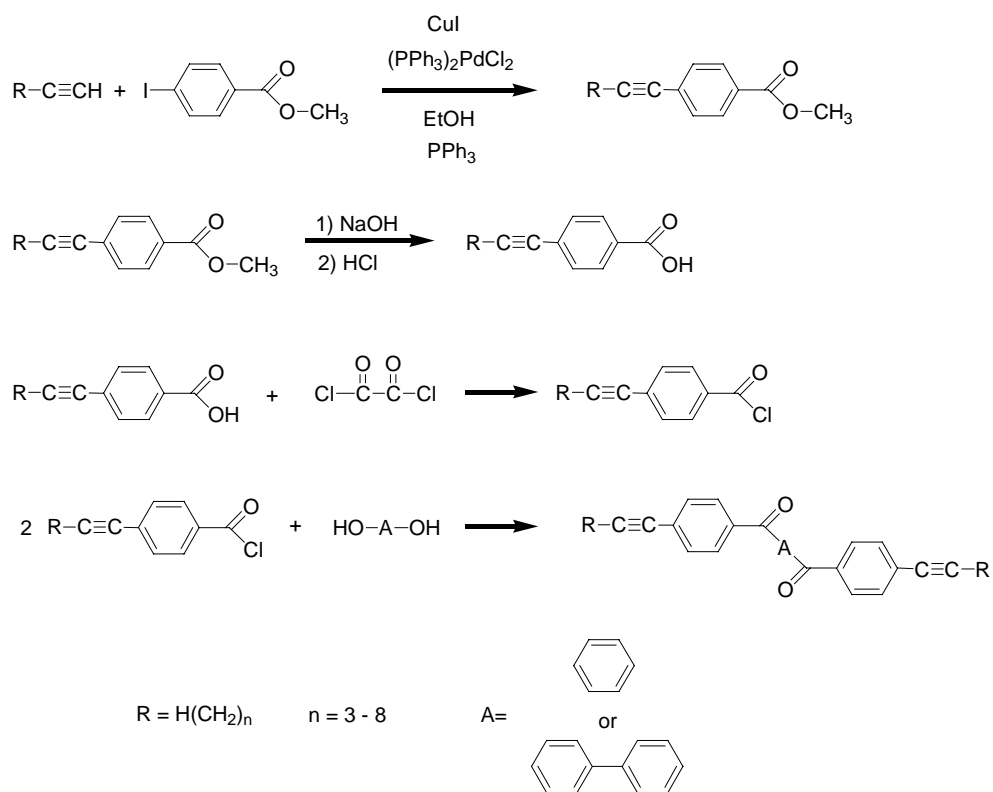
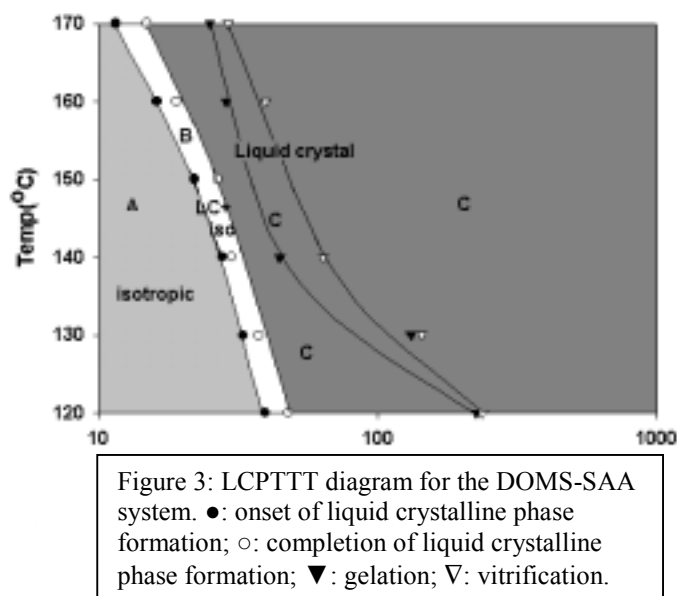


Figure 2: Scheme for synthesis of acetylene terminated LCT's.

## Cure Behavior

While there have been a variety of diagrams constructed to illustrate changes a material undergoes during isothermal curing, they are too limited for practical processing use. Traditional transformation diagrams for non-liquid crystalline materials are limited in the information they are able to display. These diagrams offer information about physical transformations during curing, but are not equipped to convey the morphological information needed for liquid crystalline materials. Other experimentally derived transition diagrams for liquid crystalline materials lack the physical information needed during isothermal processing, like gelation. Through the use of a rheometer with parallel plate geometry, a hot-stage, and a cross-polarized optical microscope, new liquid crystalline phase-time-temperature-physical transformation (LCPTTT) diagrams were constructed. These diagrams illustrate both the physical transformations and phase transitions that occur during cure, and thus provide a more general diagram describing the cure behavior of LCT's. An example of such a diagram is shown in Figure 3.

Detailed studies of the cure behavior of the nBP and nHQ monomers (Figure 1) were undertaken. The LCPTTT diagrams illustrate that the monomers change from nematic liquids to isotropic or biphasic gels during isothermal curing. However, reemergence of an ordered phase occurred if the monomers were cured at low enough temperature. The critical temperature for ordered phase retention in the final vitrified material is inversely proportional to the length of the flexible chain. This may be due to a destabilization of the liquid crystalline phases with increasing chain length. Also, as expected from the characterization of the monomers, the nBP series had greater liquid crystalline phase stability during isothermal curing than the nHQ series.



The gel times for the two series of monomers were compared for isothermal cures of 270°C. It was shown that monomers of the nHQ series reached gelation more quickly than the monomers of the nBP series with the same flexible chain length. This is attributed to a decrease in molecular mobility with increasing mesogenic unit length. Both series did show an increase in gel times with increasing chain length, however, the increase was not in a linear manner as expected. Instead, an odd-even effect was seen in both series, even though the nHQ series was cured in the isotropic phase at 270°C. This is especially surprising since traditional reasoning for this effect requires the molecules to begin in an ordered state prior to the transition to enable significant interaction between molecular endgroups. However, in this study the molecules may be maintaining localized molecular alignment that cannot be observed by POM. Also surprising was the fact that the gel times for the molecules with even flexible lengths for the nBP series did not increase significantly with increasing chain length. This shows an enhancement or leveling of the cure rate with increasing chain length, at least for chains of even length. The gel times for both series also appeared to be converging at around  $n=8$ , thus indicating the loss of the odd-even effect for monomers with chains of greater length. This is similar to the convergence seen for the clearing temperatures of the monomers.

One of the outstanding fundamental questions to be answered regarding LCT's has been how the various changes are affected by the degree of cure. For non-liquid crystalline thermosets, gelation is understood as an isoconversion phenomenon. It was unknown whether this would be true for liquid crystalline thermosets, and also what the conversion dependence would be for the liquid crystalline phase changes. By combining differential scanning calorimetry and rheology, we have now shown that gelation of DOMS/SAA is unaffected by the liquid crystalline phase, remaining an isoconversion phenomenon with gel point conversions consistent

with standard statistical models. This result indicates that the actual network formed by these molecules is unaffected by any long-range order that may be present, and is only controlled by the functionality of the individual molecules. In contrast, the isotropic to liquid crystal phase transition during cure is not an isoconversion phenomenon; rather, the transition occurs at higher conversions as the cure temperature increases. This can be understood through the increase in isotropization temperature with molecular length that occurs for liquid crystals.

### Thermal Stability

The acetylene terminated LCT phBP (Figure 1) was synthesized in order to create a system with good thermal stability, due to its all aromatic character. The monomer was a nematic thermotropic liquid crystal with a melting temperature of 268° C. The extrapolated onset of the cure exotherm occurred at 313° C. The cured thermoset retained the nematic liquid crystalline order of the parent monomer. The monomer and crosslinked resin were characterized by differential scanning calorimetry, optical microscopy, and thermogravimetric analysis. The thermal stability of the crosslinked resin was determined in both air and nitrogen at various heating rates. The onset of weight loss in air and nitrogen was determined to be 397 and 422° C respectively, for a heating rate of 10° C/min.

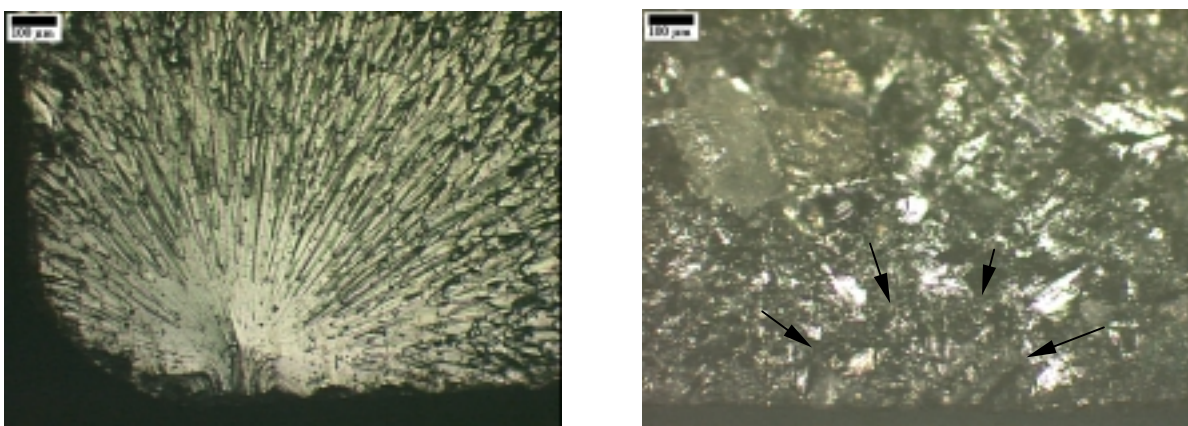


Figure 4: Optical fracture surfaces of DER383/SAA (left) and DOMS/SAA (right). Arrows indicate location of the original flaw that initiated crack growth.

### Fracture Toughness

Quantitative fractography was used as a tool to assess the effect of microstructure and chemistry on the fracture toughness of epoxies. Comparison was made between the DOMS/SAA system and the isotropic system of the diglycidyl ether of bisphenol A (DER383), also cured with SAA. Simultaneously varying two processing conditions, the temperature of cure and the amine to epoxy ratio,  $\epsilon$ , affected the DOMS/SAA system differently than the DER383/SAA system. In the liquid crystalline DOMS/SAA samples the domain size is controlled by both the temperature of cure and  $\epsilon$ ; it decreases with increasing temperature and away from stoichiometry.  $\epsilon$  also affects the chemical structure of the epoxy. These two microstructural effects compete with each other to affect the fracture toughness. At some cure conditions the effect of the domains is dominant, and at others the domains are apparently too small to affect the fracture toughness, and thus the effect of the chemical structure is dominant. The overall result is that the formation of liquid crystalline structure in the DOMS/SAA system increases the fracture toughness relative to that of a traditional epoxy at and near the stoichiometric formulation. Figure 4 shows an example, comparing the fracture surface of DER383/SAA with DOMS/SAA for the case in which the liquid crystalline domains do affect the fracture behavior.

### Moisture Effects on LC Epoxies

We have investigated the plasticization and diffusion of moisture in epoxies. The primary purpose of this work was to compare the behavior of a commercially available bisphenol A-based epoxy and an experimental liquid crystalline epoxy. Transport measurements showed that the permeability, solubility, and diffusivity of water were considerably lower in the liquid crystalline DOMS/SAA system than the isotropic DER383/SAA system.

This is expected due to the higher packing density of the molecules in the liquid crystalline phase. The diffusion coefficients were measured and related to a microstructural transport model based on the dual sorption theory. The two key microstructural aspects of the epoxies that control transport behavior are hydrogen bonding between water and the epoxy and the two phase structure of the epoxy itself. Qualitatively, the hydrogen bonding acts to fix the water molecules at polar sites in the epoxy network, slowing diffusion. In the model, this is described in terms of Langmuir sorption. With regard to the two phase morphology, the hard phase acts as a blockade against the diffusing water molecules, effectively slowing their advance. Therefore, the diffusion coefficient decreases with increasing percentage of hard-phase. In the model, this is described in terms of an additive mixing rule. The result of the model is the following expression:

$$\ln(D_{\text{eff}}(1 + R)) = V_1 \ln D_1 + V_2 \ln D_2 = (\ln D_1 - \ln D_2)V_1 + \ln D_2 \quad (1)$$

where  $D_{\text{eff}}$  is the measured diffusion coefficient,  $R$  is the ratio of hydrogen bonded to non-hydrogen bonded water,  $V_1$  and  $V_2$  are the volume fractions of the hard and soft phases, and  $D_1$  and  $D_2$  are the diffusion coefficients in the hard and soft phases. The value of  $R$  can be determined from infrared spectroscopy, as shown in Figure 5, while  $V_1$  and  $V_2$  can be determined from Tapping Mode atomic force microscopy, as shown in Figure 6. Figure 7 shows a plot based on equation 1. It is important to note that Figure 7 contains no adjustable fitting parameters; all parameters are determined from independent experiments, and thus we can conclude that this model describes the data well.

To measure plasticization in these systems, the glass transition temperatures were determined using both differential scanning calorimetry and dynamic mechanical analysis. Comparison to various models showed that the entropy model provided the best fit to the data. A model that describes the plasticization effect based on simple mixing

does not adequately describe the data, in part due to the fact that the water molecules are preferentially bound at hydrogen bonding sites in the network. However, the entropy model does account for the hydrogen bonding.

A statistical experimental design was used to determine the effect of various variables on both the amount of water absorbed and the effect that moisture had on mechanical properties. DOMS/SAA showed 25% lower moisture absorption than DER383/SAA when immersed in distilled water at 70°C. Both Young's modulus and ultimate stress were reduced by water absorption in all samples. Statistical analysis using Stat-Ease Design Expert 7.0 software revealed that interactions between cure temperature and stoichiometric ratio affect the equilibrium moisture level for both epoxies. Young's modulus is effected by the interaction between these two

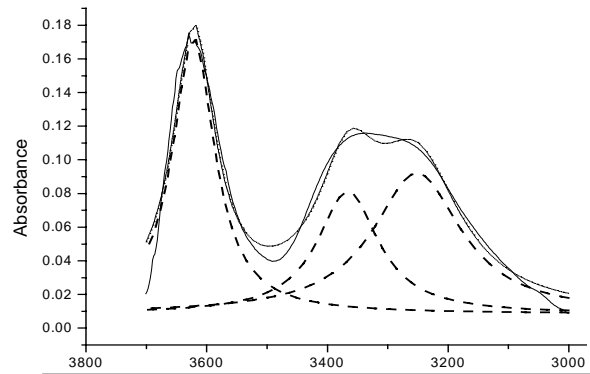


Figure 5: Infrared spectrum in the region of water absorption peaks for an epoxy. Solid line: experimental data; dashed lines: fitted peaks; dotted line: sum of the fitted peaks. The fitted peak at high wavenumbers is assigned to non-hydrogen bonded water and the two peaks at lower wavenumbers are assigned to hydrogen bonded water. Relative fractions are calculated from the relative areas of the peaks.

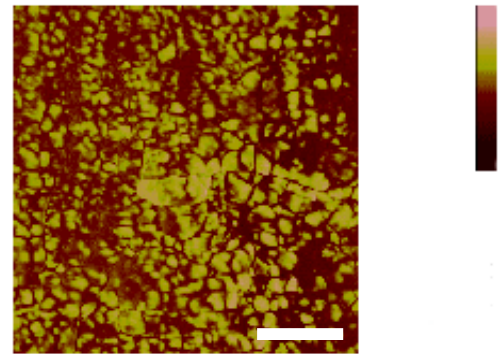


Figure 6: Tapping Mode atomic force microscopy image for an epoxy. Colors in the image correspond to different phase angles as shown in the scale on the right. High phase angles are the hard phase and low phase angles are the soft phase. Relative fractions of the two phases are calculated from the relative area of the two phases on the image. Scale bar represents 0.25  $\mu\text{m}$ .



variables as well, except in the case of fully saturated DOMS/SAA, where there is no indication that an interaction effect exists.

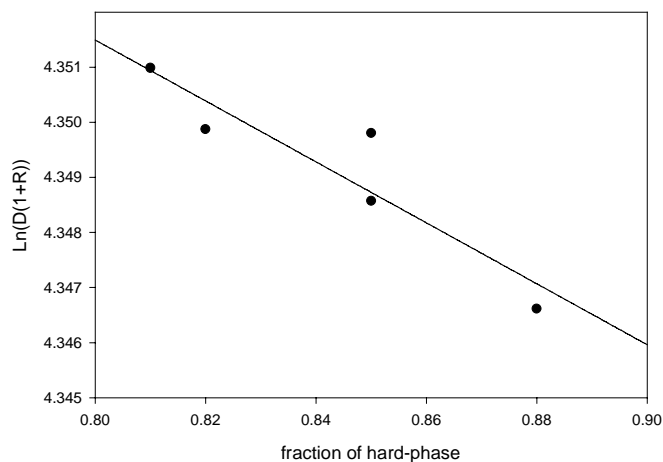


Figure 7: Fit of experimental data to equation 1. Points are the experimental data, line is a fit to the data.

## PUBLICATIONS

### Peer Reviewed Publications

Seunghyun Cho and Elliot P. Douglas, "Gelation and the development of liquid crystalline order during cure of a rigid rod epoxy", *Macromolecules*, **2002**, 35, 4550-4552

V. Ambroggi, C. Carfagna, M. Giamberini, E. Amendola, and E. P. Douglas, "Liquid crystalline vinyl ester resins for structural adhesives", *Journal of Adhesion Science and Technology*, **2002**, 16, 15-32

Jianxun Feng and Elliot P. Douglas, "Permeability of a liquid crystalline epoxy", *Materials Research Society Symposium Proceedings*, **2002**, 709, CC9.1.1-CC9.1.6

Elizabeth J. Robinson, Elliot P. Douglas, and John J. Mecholsky, Jr., "The effect of stoichiometry on the fracture toughness of a liquid crystalline epoxy", *Polymer Engineering and Science*, **2002**, 42, 269-279

Arthur J. Gavrin and Elliot P. Douglas, "Isothermal curing of acetylene functionalized liquid crystalline thermoset monomers", *Macromolecules*, **2001**, 34, 5876-5884

Arthur J. Gavrin, Christine L. Curts, and Elliot P. Douglas, "High temperature stability of a novel phenylethynyl liquid crystalline thermoset", *Journal of Polymer Science: Part A: Polymer Chemistry*, **1999**, 37, 4184-4190

David A. Langlois, Brian C. Benicewicz, and Elliot P. Douglas, "Liquid crystalline bispropargyl thermosets", *Chemistry of Materials*, **1998**, 10, 3393

### Non-Peer Reviewed Papers and Proceedings

Jianxun Feng and Elliot P. Douglas, "Plasticization of liquid crystalline and non-liquid crystalline epoxies", *Polymeric Materials: Science and Engineering*, **2003**, 88,

Arthur J. Gavrin and Elliot P. Douglas, "Synthesis of novel liquid crystalline thermosets (LCTs) and determination of their transition diagrams", *Polymeric Materials: Science and Engineering*, **2000**, 82, 346-347

Elliot P. Douglas, Arthur J. Gavrin, and Tonya Bervaldi, "Isothermal degradation of a novel phenylethynyl liquid crystalline thermoset", *Polymer Preprints*, **1999**, 40 (2), 516-517

### Meeting Presentations

Jianxun Feng and Elliot P. Douglas, "Plasticization of liquid crystalline and non-liquid crystalline epoxies", ACS National Meeting, New Orleans, LA, March, 2003

Javier Gutierrez and Elliot P. Douglas, "Liquid crystalline and non-crystalline epoxy resin moisture sorption", ACS National Meeting, Orlando, FL, April, 2002

Ryan J. Murphy and Elliot P. Douglas, "Effect of epoxy length vs. liquid crystallinity of liquid crystalline epoxy thermosets", ACS National Meeting, Orlando, FL, April, 2002

\*Seunghyun Cho, Jianxun Feng, Elizabeth J. Robinson, and Elliot P. Douglas, "Structure and properties of liquid crystalline epoxies", MRS Annual Conference, Boston, MA, November, 2001

Elizabeth J. Robinson, Jianxun Feng, Seunghyun Cho, John J. Mecholsky, Jr., and Elliot P. Douglas, "Liquid crystalline epoxies", poster presentation at International Congress of Pacific Basin Rim Societies, Honolulu, HI, December, 2000

Arthur J. Gavrin and Elliot P. Douglas, "Cure behavior of liquid crystalline thermosets", poster presentation at POLY Millennial 2000, Waikoloa, HI, December, 2000

Elliot P. Douglas, "Liquid crystalline thermosets", Massachusetts Institute of Technology, Cambridge, MA, April, 2000

Arthur J. Gavrin, and Elliot P. Douglas, "Synthesis of novel liquid crystalline thermosets (LCTs) and determination of their transition diagrams", American Chemical Society National Meeting, San Francisco, CA, March, 2000

Elliot P. Douglas, Arthur J. Gavrin, and Tonya Bernaldi, "Isothermal degradation of a novel phenylethynyl liquid crystalline thermoset", ACS National Meeting, New Orleans, LA, August, 1999

#### **Publications Submitted but Not Yet Published**

Jianxun Feng, Kenneth R. Burger, and Elliot P. Douglas, "Water vapor transport in liquid crystalline and non-liquid crystalline epoxies", *Journal of Materials Science*, submitted

#### **SCIENTIFIC PERSONNEL**

Stephanie DiFrancesco; current graduate student, funding from Motorola

Susan Leander; current graduate student

Luwei Bu; current graduate student

Seunghyun Cho; Ph.D. received July, 2002

Jianxun Feng, Ph.D. received December, 2001

Michael Steenhoek, undergraduate senior thesis, May, 2001

Javier Gutierrez, undergraduate, June, 2001 – April, 2002

Ryan Murphy, undergraduate senior thesis, May, 2002

Tonya Bernaldi, non-thesis M.S. received December, 2000, funding from University of Florida College of Engineering

Elizabeth Oborn, M.S. received September, 2000

Arthur Gavrin, Ph.D. received August, 2000

Pere Castell, visiting graduate student from Spain, September, 2000 – November, 2000

Veronica Ambrogi, visiting graduate student from Italy, September, 1998 – November, 1998

Christine Curts, undergraduate, May, 1998 – August, 1998